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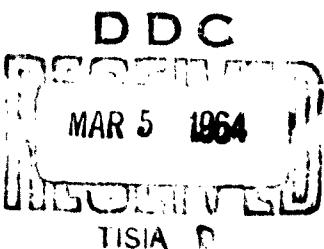
THE INFRARED SPECTRA OF
RUBIDIUM BORATES OF
VARYING COMPOSITION

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ABSTRACT

The infrared transmission spectra of a series of rubidium borates consisting of varying proportions of rubidium oxide and boron oxide have been studied in the 2.5 to 15.5% range. The rubidium oxide concentration varied from 4.2 to 50 mol %. Frequency assignments were made for molecular groups in these rubidium borates.

The results can be interpreted to indicate that an increasing proportion of trigonally coordinated boron atoms in the borate glass network structure became tetrahedrally coordinated as the Rb₂O content was increased up to 33 mole %. This was accompanied by a simultaneous increase in the concentration of terminal >B-O⁻ groups. Glasses containing Rb₂O in excess of 33 mole % tended to devitrify as boron reverted to trigonal coordination. At 50 mole %, the rubidium metaborate structure resembled that of sodium metaborate. Selected metal oxides, introduced into glasses of high Rb₂O content, entered into complex formation with >B-O⁻ groups to reconstitute the network structure of the glass.

SUMMARY

The Problem

The structure of the alkali borates varies with composition. Although numerous investigators have employed different methods to study the alkali borate system, their interpretations of experimental data have not resulted in any general agreement concerning the nature and extent of the structural variations. Conflicting hypotheses make difficult the application of any one theory for the structure of alkali borates to rubidium borates being studied at this laboratory.

Findings

A series of rubidium borates containing up to 50 mole % has been studied by infrared spectroscopy. The transmission spectra indicate a continuous variation in borate structure up to at least 28 mole % Rb₂O content with no discontinuity occurring at 17 mole %. The spectra resemble those of sodium and lithium borates.

From an interpretation of the data, it was concluded that the coordination number of some boron atoms changes from 3 to 4 and then reverts again to 3 with increasing Rb₂O content in the borate. Simultaneously the rubidium borate is transformed from the vitreous state to the crystalline state. Reversal of these states can be effected by the introduction of selected metal oxides.

INTRODUCTION

The addition of alkali oxides to vitreous boron oxide produces marked changes in the physical properties of borate glasses. These changes are generally attributed to alteration of the boron oxide structure through conversion of the normally trigonal coordination of boron to tetrahedral coordination. Although most investigators agree that a coordination change occurs, they do not agree on the borate composition at which the conversion process ceases. The range of compositions over which disagreement exists is from approximately 11 to 33 mole % alkali oxide content, with the 17 mole % concentration appearing to be a particularly controversial region. When tetrahedrally coordinated boron formation ceases, boron-oxygen bonds supposedly cleave to form $\text{B}-\text{O}^-$ groups.

Borate glasses tend to devitrify as the alkali oxide content exceeds 33 mole %. However, no systematic study has been made of intermediate borate compositions between 33 mole % and that of crystalline metaborate at 50 mole %.

This investigation was undertaken with the object of reconciling the different views concerning the relationships between composition, structure, and coordination change. The borates of rubidium, which were studied by infrared spectroscopy, had a maximum Rb_2O concentration of 50 mole %. The information obtained supplements data from vapor pressure measurements¹ already completed for the liquid rubidium borate system.

Background

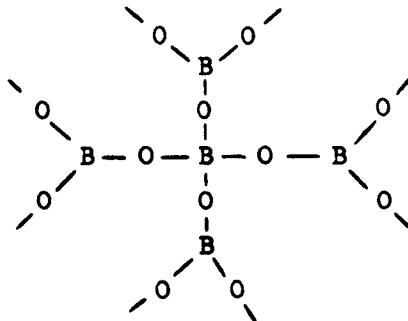
Zachariasen² has postulated the structure of vitreous boron oxide to be a random, three-dimensional network in which trigonally coordinated boron atoms are joined coplanarly to oxygen atoms, with these oxygen atoms forming bridges to other boron atoms.

Biscoe and Warren³ used X-ray diffraction to study sodium borate glasses of different sodium oxide content. They found that the average

boron-to-oxygen distance in the borate increases with increasing sodium oxide. This was ascribed to a change from three to four in the coordination number of some boron atoms. Correlating this change with the thermal expansion data of Gooding and Turner,⁴ they concluded that the formation of tetrahedrally coordinated boron ceases when the borate glass contains approximately 17 mole % sodium oxide. They also concluded that sodium oxide in excess of this concentration causes rupture of glass network bonds, with the result that some of the oxygen atoms that were formerly bonded to two boron atoms then become bonded to only one boron.

Krogh-Moe⁵ did not fully accept the Biscoe and Warren interpretation of the thermal expansion curve. He stated that an alternate interpretation may also be used. That is, two opposing effects may be at work when alkali oxide is added to boron oxide. One is that the structural configuration of boron oxide, which has a relatively high coefficient of expansion, is destroyed upon addition of alkali oxide. This lowers the coefficient of expansion. On the other hand, the addition of alkali oxide itself tends to increase the coefficient of thermal expansion. Superposition of the two effects results in the observed minimum in the thermal expansion curve at approximately 17 mole % alkali oxide concentration.

Tosio Abe⁶ postulated that when the sodium borate glass contains 17 mole % Na_2O , one-fifth of the boron atoms are tetrahedrally coordinated. The glass is composed of structural units, each consisting of a single, tetrahedrally-coordinated boron joined to four trigonally coordinated borons via oxygen bridges:



Like Biscoe and Warren, Abe also believed that the formation of tetrahedrally coordinated boron stops at 17 mole % Na_2O , and that Na_2O in excess of this concentration severs the boron-oxygen bonds that connect these structural units to one another.

In a later work, Huggins and Abe⁷ revised Abe's original structural theory and concluded that tetrahedrally coordinated boron atoms are formed only in borate glasses that contain a maximum of 11 mole %

alkali oxide. At concentrations greater than this, the concentration of tetrahedrally coordinated borons slowly diminishes.

Taking a still different view, Krogh-Moe⁸ and Zhdanov⁹ pointed out that there is experimental evidence to show that boron atoms of tetrahedral coordination continue to be formed until the borate glass is at least 33 mole % in alkali oxide. The nuclear magnetic resonance work of Silver and Bray¹⁰ and of Svanson, et al.,¹¹ apparently confirm this.

Other investigators who employed infrared spectroscopy for the study of the alkali borates also have not concurred in the interpretation of their experimental results. Anderson, et al.,¹² concluded from their studies that the addition of Na₂O to B₂O₃ yields a close-knit network of (B₉O₁₄)-complexes, but Krogh-Moe¹³ indicated that their samples were contaminated by water. Moore and McMillan¹⁴ analyzed thin films of sodium borate glasses and claimed their results were in agreement with Biscoe and Warren's theory of tetrahedrally coordinated boron saturation at approximately 17 mole % Na₂O content. However, their thin borate films were also altered by absorbed atmospheric moisture, according to Parsons and Milberg.¹⁵ Jellyman and Procter¹⁶ used a reflectance technique to study sodium borate glasses in bulk form, and they too, claimed agreement with Biscoe and Warren's postulate. On the other hand, Borelli, et al.,¹⁷ who made a comparative study of the spectra of sodium borates obtained by different sample preparation techniques, could find no evidence to support the Biscoe and Warren theory. Krogh-Moe¹³ has also presented results of his comparative studies of vitreous and crystalline borates to argue against tetrahedrally coordinated boron saturation at 17 mole % Na₂O concentration.

It can be seen that investigators attach importance to establishing the composition at which tetrahedrally coordinated boron formation ceases because they relate this composition to subsequent structure changes. Agreement is lacking.

Approach

The infrared spectra of the many investigators of sodium and lithium borates are well documented, and numerous spectral interpretations have been made. Both the spectra and their interpretations provide a good background for this study of rubidium borates by infrared spectroscopy.

Since investigators have found that the structures of boron oxide glass and alkali borate glasses are altered by the sorption of atmospheric moisture to yield additional spectral absorption bands attributable to boric acid, the spectra of boron oxide in progressively hydrated stages were first obtained for reference and for detecting possible interference due to these bands.

Next, the spectra of rubidium borates of different compositions were obtained. Spectral interpretation was based on empirical relationships which exist between molecular structure and spectral characteristics. Correlations were made by comparison or by analogy with known spectra.

Spectral intensity measurements were made to detect any change in relative rates of growth for different molecular groups. The determination of absolute absorption intensities of molecular groups in the borates is impracticable because of difficulties in reproducing very thin infrared-transparent samples of the same thickness, and in establishing the specific absorbance of each molecular group. Moore and McMillan¹⁴ circumvented these problems by comparing the ratio of extinction coefficients for the absorption bands in one sample against a corresponding ratio of a different sample. A similar technique is employed in this work using extinction ratios, as these are proportional to the ratios of bond abundances, or concentration.

The spectra of rubidium borate glass containing selected metal oxides were examined to check the postulate¹ that the introduction of these oxides reverses the tendency of the glass to devitrify. Spectral changes reflecting changes in structure should be observable in the infrared spectrum.

EXPERIMENTAL PROCEDURE

The materials for preparation of the rubidium borates were analytical reagent grade boric acid obtained from the J. T. Baker Co., and rubidium carbonate which was obtained from the A. D. Mackay Co. and from K & K Laboratories.

The boric acid was heated in a platinum dish over a Meker burner until the expulsion of water was complete. The resulting boron oxide melt was transferred to an electric furnace and heated for several hours at 1000°C, then allowed to cool in a desiccator. The Rb₂CO₃ was purified by dissolving in distilled water, filtering, and recrystallizing. Spectrochemical analysis showed that the purified Rb₂CO₃ contained less than 1 % impurities of other alkali metals. It is believed that these impurities did not materially affect the rubidium borate spectra.

Rubidium borates of different compositions were prepared by fusing together known amounts of crushed B₂O₃ glass and Rb₂CO₃ in a platinum crucible until CO₂ was completely expelled from the melt. The

compositions were checked by titrimetric analysis. Thoroughness of CO₂ expulsion was checked by dissolving the borates in dilute acid solution.

The spectra of B₂O₃ and rubidium borates of low Rb₂O content - 4.2, 11, 20, 28, and 33 mole % - were obtained by infrared transmission through thin glass films. This method involved minimum handling of material and was free of matrix interference. The films were formed by the procedure of Moore and McMillan¹⁴ in which molten boric oxide or borate glass was collected on the tip of a 5-mm pyrex tubing and a thin-walled bulb was formed by blowing with dry air. A section of the blown film was mounted over a closed wire loop which had been previously dipped in a Canada balsam-xylol solution. The preparation was immediately analyzed to minimize atmospheric hydration effects. The thickness of the films is estimated to be less than one micron.

The spectra of rubidium borates of high Rb₂O content - 33, 41, and 50 mole % - were not obtainable by the same method, because melts of these borates were of lower viscosity and they had a tendency to crystallize upon solidification. Therefore, borate mulls with the consistency of thin paste were formed by crushing and grinding the borates with agate mortar and pestle in the presence of Nujol, a purified mineral oil. A small amount of mull was squeezed between two rock salt plates. The plates were separated and one was arbitrarily selected for analysis after most of the Nujol had been removed by blotting.

Intentional overlap of the two sample preparation techniques at 33 mole % Rb₂O was made in order to determine whether differences exist in the spectra of borate samples prepared by the two techniques.

Three component systems consisting of various complex-forming metal oxides and Rb₂O-B₂O₃ mixtures were prepared by fusing these materials together in a platinum crucible. Thin films were prepared, and their spectra were obtained in the manner used for the other borate glasses.

A Perkin-Elmer double-beam infrared spectrometer, Model 21, was used for the analyses. All spectra were obtained in the rocksalt prism region of 2.5 to 15.5 μ .

PRESENTATION OF DATA

The Spectra of Pure and Hydrated B₂O₃

Before the spectra of rubidium borates are interpreted, the effect of contaminating moisture on a sample needs to be accounted for. To

determine this effect, the spectra of a thin film of B_2O_3 in progressive stages of hydration were obtained (shown in Fig. 1 as curves b, c, d, and e). By graphically eliminating from these curves absorption bonds due to the effects of water, the curve a was obtained. (All curves are displaced vertically to facilitate comparison.)

Curve a represents a hypothetical infrared spectrum of anhydrous B_2O_3 glass. It shows peaks only at $8\ \mu$ and $13.9\ \mu$, respectively corresponding to the in-plane and out-of-plane vibrations of planar BO_3 molecular groups comprising the B_2O_3 glass network. This spectrum is supported by the work of MacKenzie, et al.,¹⁸ who show that absorption bands which occur at $3.2\ \mu$ and $6.9\ \mu$ for ordinary, slightly hydrated B_2O_3 (curve b) disappear upon dehydration at elevated temperatures. It is also in agreement with the vibrational spectrum obtained by Parsons and Milberg¹⁵ for B_2O_3 glass films.

Curve b represents the absorption spectrum of the vitreous B_2O_3 used as a starting material for preparation of the borates. Despite rapid sample manipulation and subsequent analysis in a dry atmosphere, hydration effects are evident. Continued hydration of the same sample yields the spectra shown in curves c, d, and e. Curves c and d represent intermediate mixtures of starting material and final product.

Curve e represents the spectrum of the completely hydrated final product. The spectrum is similar to that obtained by other investigators¹⁹⁻²¹ for orthoboric acid, H_3BO_3 . Of particular note is the fact established by these investigators that the $6.9\text{-}\mu$ absorption band is due to vibration between the boron and hydroxyl group, $B-(OH)$. This information is useful in later interpretation of rubidium borate spectra. Growth of the $B-(OH)$ group can result from the rupture of boric oxide glass network bonds in the presence of water vapor in the following manner: $\text{B-O-B} + H_2O \rightarrow 2 \text{B-(OH)}$. Hence, the $6.9\text{-}\mu$ band grows at the expense of the $8\text{-}\mu$ band.

Spectra of Rubidium Borates

Figure 2 shows the variations in transmission spectra for the thin films of " B_2O_3 " and rubidium borate glasses. Quotation marks about B_2O_3 denote the very slightly hydrated nature of the starting material. The other borates in the figure are also hydrated to lesser degrees, as shown by the absorption at $3.1\ \mu$, but their basic spectra do not appear to be materially affected by moisture.

The spectral variations of the rubidium borates resemble those obtained for sodium borates.^{16,17} As in the hydration series shown in Fig. 1, the $7\text{-}\mu$ band grows at the expense of the $8\text{-}\mu$ band with successive additions of Rb_2O . It also migrates to $7.5\ \mu$. It is noted that the

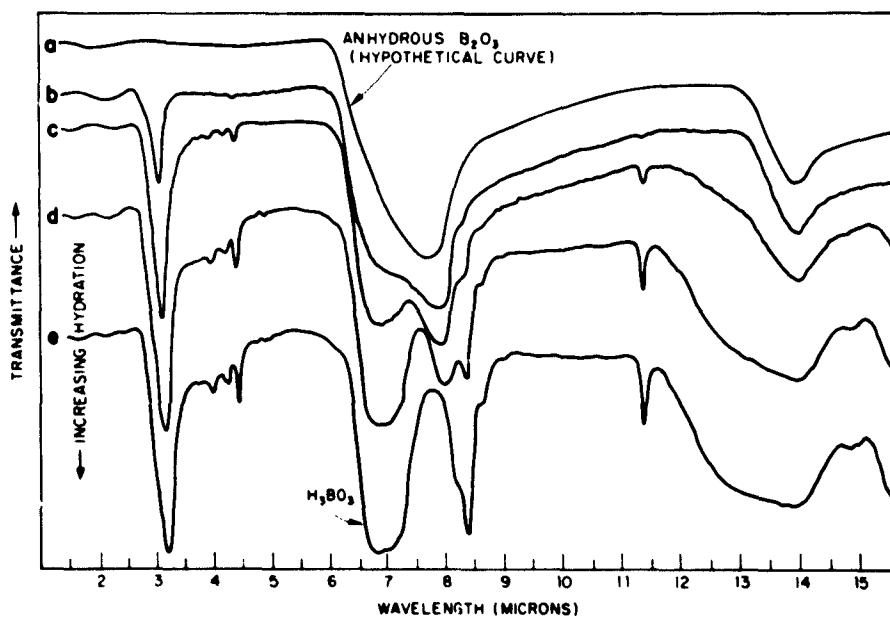


Fig. 1 Infrared Transmission Spectra of Progressively Hydrated Boric Oxide

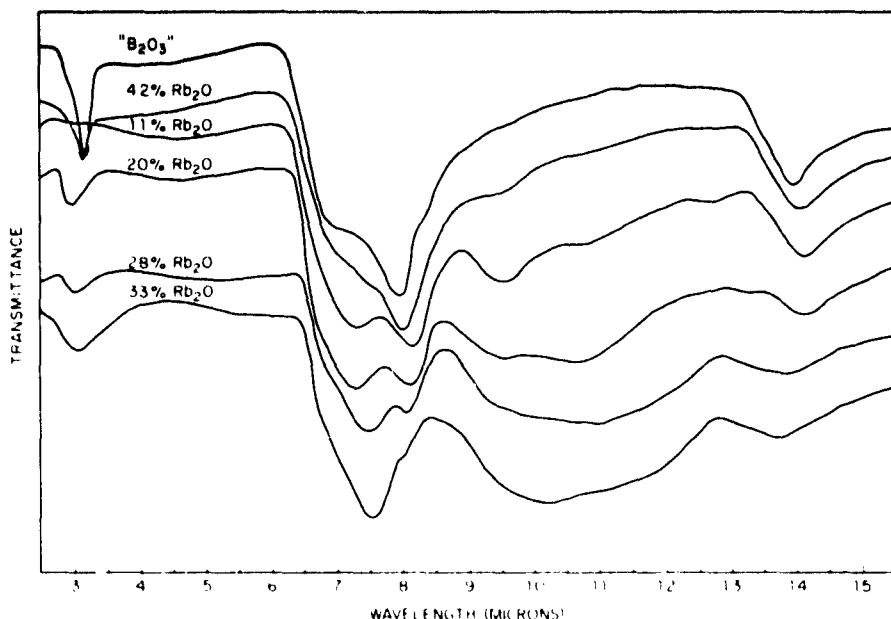


Fig. 2 Infrared Transmission Curves for Thin Film B₂O₃ and Rubidium Borate Glasses

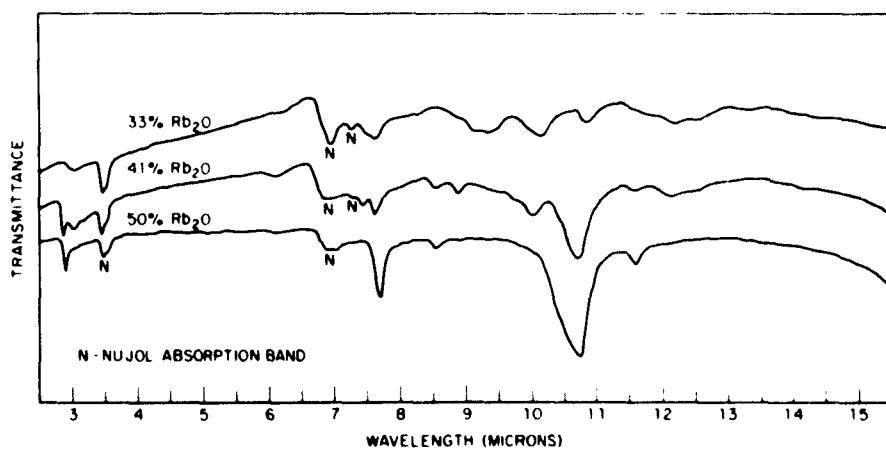


Fig. 3 Infrared Transmission Curves for Rubidium Borates of High Rb₂O Content Prepared by the Nujol Method

absorption intensity of this band, relative to the 8- μ band, increases much more rapidly between 28 and 33 mole % than any other two concentrations. At 4.2 mole % Rb₂O content, a 9.5- μ band emerges which grows and remains prominent up to 33 mole %. At 11 mole %, another emerges at 10.7 μ and grows in a similar manner. These last two bands are broad and overlapping, so their resolution varies from fair to poor.

Figure 3 shows the spectra of rubidium borates of high Rb₂O content prepared by the Nujol mull method. The spectrum of borate glass of 33 mole % Rb₂O differs from that obtained in Fig. 2. Its strong resemblance to that of crystalline K₂B₄O₇·5H₂O²² suggests that the mulled sample is more hydrated. When the Rb₂O content of the borate is increased to 50 mole %, some of the bands disappear. The resulting spectrum of crystalline rubidium metaborate is identical with that of sodium metaborate.²²

Determination of Extinction Ratios

The object of plotting spectral intensity measurements versus rubidium borate composition is to detect unexpectedly rapid changes in borate structure. Intensity measurements of traces in Fig. 2 are made by setting each trace at 6 μ on a base line of total transmittance (zero absorption). The transmittance, T, of each absorption band is recorded and the extinction value, E, is calculated with the aid of the following equation:

$$E = \log \frac{1}{T} = kcd$$

where E = extinction (also called absorbance)

T = transmittance of the sample

k = specific extinction coefficient; extinction at unit concentration and unit sample thickness

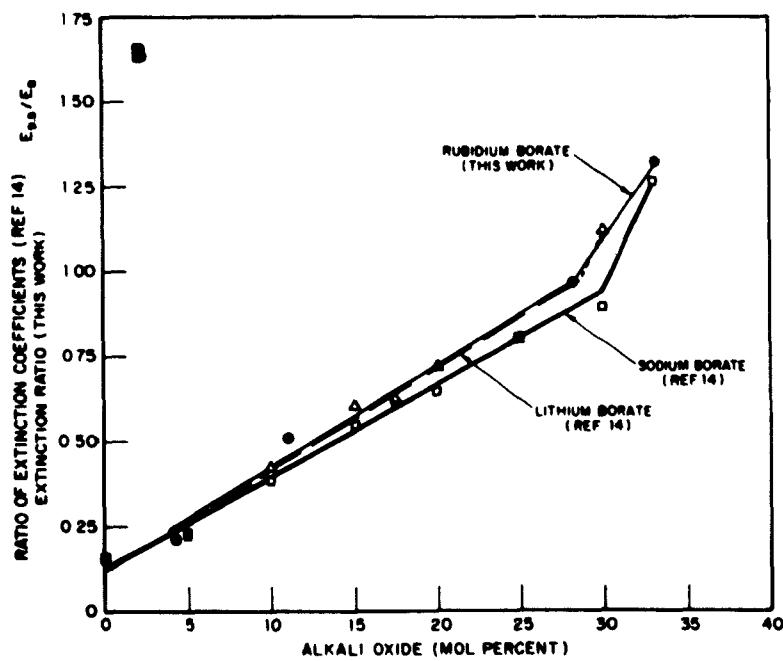
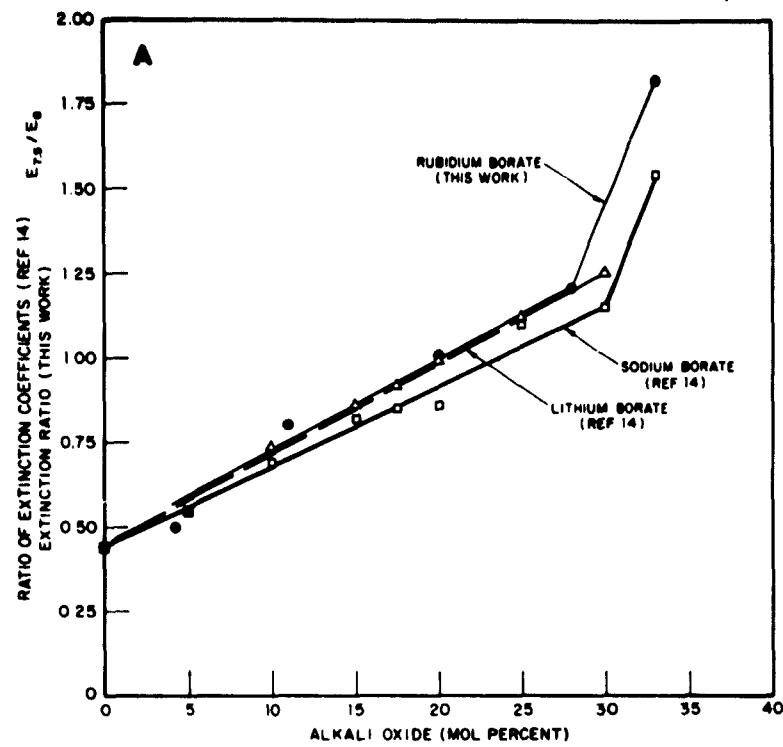
c = concentration of the absorbing molecular group

d = thickness of the sample, or absorption path length

For a given borate sample, the relative extinction of a given band at a particular wavelength, E _{λ} , and that of a reference band, E_{ref}, has the following relationship:

$$\frac{E_{\lambda}}{E_{ref}} = \left(\frac{k_{\lambda}}{k_{ref}} \right) \left(\frac{c_{\lambda}}{c_{ref}} \right) = K \frac{c_{\lambda}}{c_{ref}}$$

where k equals k _{λ} /k_{ref}. The extinction ratio is therefore proportional to the relative concentrations of the respective molecular groups. Uniform changes in extinction ratios when plotted against borate composition yield points which lie on the same straight line. Abrupt changes in ratios, or relative concentrations, give a sharp change in slope of that line.



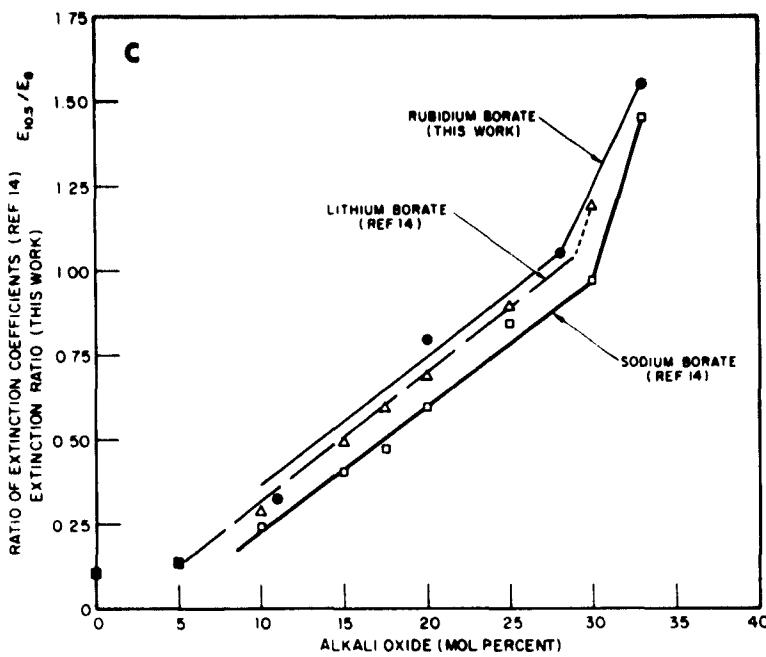


Fig. 4 Comparisons of Variations in Extinction Ratios for Rubidium Borate of This Study and in Extinction Coefficient Ratios for Lithium and Sodium Borates.¹⁴ All ratios are plotted against alkali oxide content.

Extinction Ratios:

- A - $7.5 \mu : 8 \mu$
- B - $9.5 \mu : 8 \mu$
- C - $10.5 \mu : 8 \mu$

The four spectral bands of interest are at 7.0-7.5, 8.0-8.2, 9.5, and 10.5-10.7 μ (Figs. 2 and 3). Some absorption peaks differ slightly in wavelength from one composition to another, but there is sufficient separation among bands to introduce no confusion.

In the determination of all extinction ratios, the 8.0-8.2 μ band is chosen as reference since it alone diminishes in intensity as the others increase. Values of these ratios versus rubidium borate composition are plotted (dark circles) in Figs. 4A, 4B, and 4C. Re-calculated ratios of extinction coefficients for the absorption bands obtained by Moore and McMillan¹⁴ for lithium borates (triangles) and sodium borates (squares) are plotted in the same figures for comparison. No change in slope of the lines is noted between the critical region of 10 and 20 mole % alkali oxide concentration, but a sharp one occurs at approximately 28 to 30 mole %. These characteristics are present in all the plots of Figs. 4A, 4B, and 4C. Discussion of relative spectral intensities is deferred to a later section.

Spectra of Borates Containing Added Complex-forming Metals

If certain metal oxides are capable of entering into complex-formation with molecular units in borate glass, i.e., if the metals act as electron acceptors to form dative bonds with the negatively charged oxygen of the $\text{B}-\text{O}^-$ groups to reconstitute the glass network, then diminished intensity should be observable for the absorption band assigned to these units. To study this effect, 5 atom % of the metal oxides - Nb_2O_5 , MoO_6 , V_2O_5 , TiO_2 , ZnO - were each fused into a set of rubidium borate samples containing initially 11, 28, and 33 mole % Rb_2O . The resultant borate compositions respectively contained, on an atomic basis, 10.5 % Rb:84.5 % B; 26.6 % Rb:68.4 % B; and 31.3 % Rb:63.7 % B.

The transmission spectra of rubidium borate glasses containing added metal oxides are shown in Figs. 5A, 5B, and 5C. Of interest here are the relative intensities of the two absorption bands at 7.4 μ and 8.2 μ . These bands have been assigned, respectively, to the $\text{B}-\text{O}^-$ group and the BO_3 glass network.

Figure 5A shows absorption curves of the initial borate glass containing 11 % Rb_2O and succeeding curves for this glass to which were added 5 atomic % of Nb, Mo, V, and Ti, respectively. It is seen that the relative intensities of the 7.4- μ and 8.2- μ peaks are unaffected by the addition of these metals.

Figure 5B shows the absorption curves of borate glass containing 28 % Rb_2O , and other curves for the same glass to which 5 atom % Zn, Mo, and V were added. Although the relative intensities of the 7.4- μ and 8.2- μ peaks do not appear to be affected by ZnO , the added MoO_3 and V_2O_5 have a substantial effect.

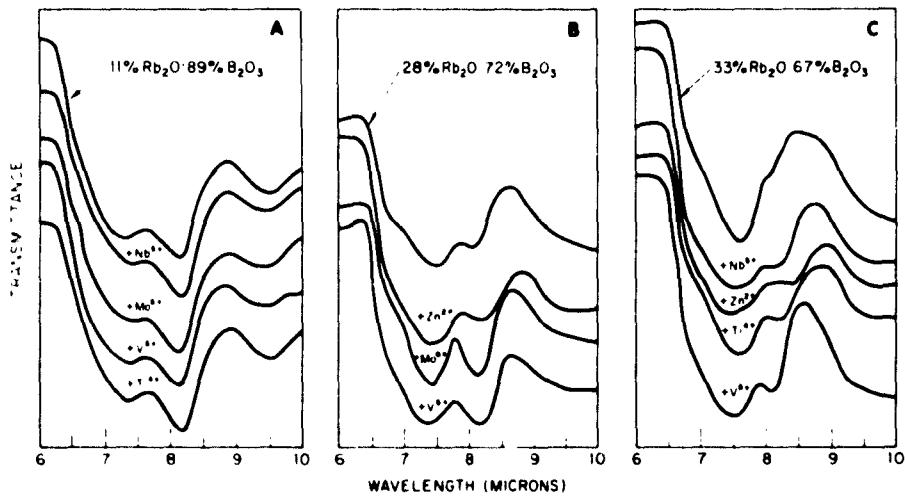


Fig. 5 The Effect of 5 Atom % Metal Ions on the Spectra of Borate Glasses of Different Rb_2O Content

Figure 5C shows that, with respect to the 8.2- μ peak, the very strong 7.5- μ borate peak of 33 mole % Rb₂O is sharply reduced in intensity with the addition of any of the complex-forming metal oxides.

DISCUSSION

Wavelength Assignments to Molecular Groups

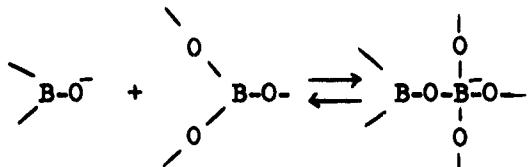
Since infrared-absorption wavelengths correspond to vibrational energies about equilibrium positions of atoms belonging to different molecular groups, the spectra of Fig. 2 show progressive growth of several groups in borate glasses of increasing Rb₂O content. It has already been seen that in the region of 7 to 8 μ , a process develops from the outset which is similar to that which occurs in the hydration of B₂O₃, i.e., a 7-7.5- μ band grows as the 8-8.2- μ band recedes. Whereas the hydration products of B₂O₃ are >B-OH molecular groups, the analogous products in this case are terminal >B-O⁻ groups: >B-O-B< + O⁻ \rightarrow 2 >B-O⁻. The vibrational frequency between boron and oxygen in both products should be nearly the same. On this basis, the 7-7.5- μ absorption band is assigned to the >B-O⁻ vibration. Contrary to the postulate of Biscoe and Warren,³ this reaction occurs in a borate whose alkali oxide concentration is less than 17 mole %.

Another effect of adding Rb₂O to B₂O₃ glass is the formation of tetrahedrally coordinated boron. A new absorption band should be in evidence. The location of this band may be inferred from a finding by Dachille and Roy²³ who noted that when germanium oxide changes from the quartz form to the rutile form, germanium coordination changes from 4 to 6. This change is reflected in a shift of the main stretching vibration to a lower frequency. They found that the ratio of the coordination numbers are related by the ratio of the squares of the respective absorption wavelengths and may be expressed by the following equation:

$$\frac{6}{4} = \left(\frac{\lambda_6}{\lambda_4} \right)^2 .$$

The empirical rule of Dachille and Roy may be applied to calculate the expected energy of the tetrahedrally coordinated boron-oxygen vibration. With 8.1 μ as the absorption wavelength for trigonally-coordination boron, absorption by tetrahedral boron should occur at 9.5 μ . Such a band does appear in the spectrum, so a reasonable assignment can be made.

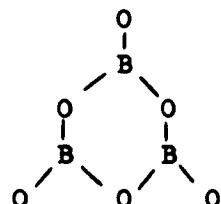
The formation of the tetrahedral structure can be represented by the equilibrium reaction of B-O^- with a trigonally coordinated boron:



The spectra of Fig. 2 show that some B-O^- groups always remain uncombined, so that there is coexistence of BO_3^- , BO_4^- , and B-O^- groups in the glasses. At elevated temperatures, the equilibrium is probably shifted to favor BO_3^- and B-O^- groups.^{1,24}

In addition to the two processes involving the formation of B-O^- and BO_4^- groups, a third may be evidenced by the $10.5-10.7-\mu$ band. This band is first prominent in the spectra at 20 mole % rubidium oxide content (Fig. 2). It is still present at 33 mole %, although it is not as well resolved. In order to obtain a clue to this vibrational mode, it is necessary to examine borate spectra of higher alkali content.

Rubidium metaborate (RbBO_2) formed by fusing together equimolar quantities of Rb_2CO_3 and B_2O_3 yielded the absorption spectrum shown in Fig. 3 for 50 % Rb_2O content. This spectrum is identical with the one for crystalline sodium metaborate.²² It may be expected that these metaborate structures would be similar to that of potassium metaborate, whose negative radical, as described by Zachariasen,²⁵ consists of a six-membered boroxol ring:



Evidently, the alkali ions exert little, if any, influence on this borate structure.

Although the boroxol ring has been found to exist in a borate of high Rb_2O content, little thought has been given to its possible existence at low Rb_2O concentrations. However, Krogh-Moe⁵ believes that many trigonally coordinated borons in the glass do condense into such hexagons even at low alkali oxide concentrations, although he has offered no evidence for this. If the principal absorption band of RbBO_2

at 10.7 μ in Fig. 3 can be attributed to the boroxol structure, then it can be seen that this ring might possibly be present in borate glasses of Rb_2O content as low as 11 mole %.

The other prominent peak (in Fig. 3) of the metaborate at 7.6 μ should correspond to the 7.5- μ peak assigned to terminal B-O^- groups. No absorption band attributable to tetrahedrally coordinated boron is present in alkali metaborate.

The assignment of absorption wavelengths to the various structural groups are given in Table 1. Assignments made by two other groups of investigators are compared. There is complete accord in the assignment of the 8- μ band and the broad 13.9-14.5- μ bands to the BO_3 vibrations, and the 9.5- μ band to the BO_4^- vibration. The 6.9- μ band obtained by Moore and McMillan is actually a boric acid band.

By analogy with the H_3BO_3 spectra, the 7-7.5- μ band in this work was assigned to the B-O^- vibration. But this same vibration was assumed by Jellyman and Procter, without substantiation, to evidence absorption between 10 μ and 12 μ . On the other hand, Moore and McMillan failed to consider the possibility of detecting this molecular group even at higher Na_2O concentrations.

In addition to the 9.5- μ band, the other investigators^{14,16} assigned other bands (7-7.5 μ , 10.5 μ) to the BO_4^- group because they appeared together in the same spectra. This does not seem to be fully justified.

Because of its prominence in the metaborate spectrum, the 10.7- μ band is assigned to the vibrational characteristics of the boroxol group. Neither of the other two teams of investigators considered the presence of this group in the borate glasses.

The data from infrared absorption spectra (Figs. 2 and 3) of the rubidium borates are given in Table 2. Indicated in the table are the presence or absence of absorption bands at the various wavelengths and the molecular group associated with each wavelength. Since each spectrum was obtained from a separate sample preparation, there is no uniformity of sample thickness.

Changes in the rubidium borate glass structure with composition can be described in terms of four absorption wavelengths - 7-7.5 μ , 8-8.2 μ , 9.5 μ , and 10.5-10.7 μ , corresponding respectively to absorption by B-O^- , BO_3 , BO_4^- , and boroxol groups. Except for the absence of boroxol-group absorption in the glass of 4.2 mole % Rb_2O , all groups were present in all the rubidium borate glasses.

TABLE 1
Comparison of Wavelength Assignments of the Structural Groups

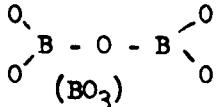
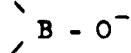
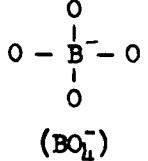
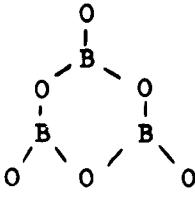
Structural Group	Type of Vibration	Wavelength (μ)		
		This Work	Jellyman and Proctor ¹⁶	Moore and McMillan ¹⁴
 (BO_3)	stretching	8	8	8
	bending	13.9	14-14.5	13.9
			6.9	
	stretching	7-7.5	10-12	(not considered)
 (BO_4^-)	stretching	9.5	7-7.5	7.5
			9.5	9.5
			10.5	
 (boroxole)	not specified	10.7	(not considered)	(not considered)

TABLE 2

Infrared Absorption at Various Rb_2O Compositions

Preparation Method	Mole % Rb_2O	$\text{B}-\text{O}^-$	$\text{B}-\text{O}-\text{B}$	BO_4^-		$\text{B}-\text{O}$
		7.5 μ	8 μ	9.5 μ		
Glass Films (see Fig. 2)	0*	x**	x	o		o
	4.2	x	x	x		o
	11	x	x	x		x
	20	x	x	x		x
	28	x	x	x		x
	33	x	x	x		x
Nujol (see Fig. 3)	33	x	(?)	x		x
	41	x	o	o		x
	50	x	o	o		x

x = absorption

o = no absorption

* B_2O_3 ** H_2O contamination

The rubidium borates analyzed by the Nujol preparation method show no \rangle B-O-B \langle network vibration at $8\ \mu$. All show \rangle B-O \langle and boroxol vibrations. The BO_4^- vibration at $9.5\ \mu$ is present only up to 33 mole % Rb_2O . The inconsistency of spectra at 33 mole % between the two sample preparation methods has already been mentioned in a previous section.

Structural Models

According to the interpretation of spectra in this work, rubidium borate glasses contain a mixture of several molecular groups. Except at very low Rb_2O concentrations, structural models of borate glasses should embody all of these groups. Some models are proposed here which are compatible with the observed spectra.

As was mentioned before, vitreous B_2O_3 is considered to be a random three-dimensional network of trigonally coordinated boron atoms joined by oxygen atoms. Figure 6a is a two-dimensional representation of this network. As oxide is added, via Rb_2O , to this network, \rangle B-O-B \langle bonds are cleaved to form \rangle B-O \langle groups. Some of these groups join with trigonally coordinated borons to form tetrahedrally coordinated borons. Boroxol groups are also present, and their presence becomes more apparent at higher rubidium oxide concentrations. The resulting effect on the glass network is depicted in Fig. 6b, where $x\text{Rb}_2\text{O}$ in the caption denotes some arbitrary concentration between 11 and 33 mole % Rb_2O .

The absorption spectra shown in Figs. 2 and 3 indicate that accelerated changes occur at Rb_2O concentrations in excess of 28 mole %. Devitrification evidenced by diminished BO_3^- absorption at $8\ \mu$ is accompanied by rapid growth of \rangle B-O \langle ($7-7.5\ \mu$), BO_4^- ($9.5\ \mu$), and boroxol ($10.7\ \mu$) groups. Considering that the possibility exists for one of the borons in a boroxol ring to become tetrahedrally coordinated, the simultaneous transformation of the structure shown in Fig. 6c to structures shown in Fig. 6d and upon further addition of Rb_2O to Fig. 6e will satisfy the conditions for concurrent growth of these molecular groups. The structural unit of Fig. 6d resembles that postulated by Morimoto²⁶ for crystalline tetraborate which contains two tetrahedrally coordinated boron atoms. The addition of more Rb_2O to the borate composition in Fig. 6c may result in fracture of tetrahedral bonds to yield \rangle B-O \langle and boroxol groups as shown in Fig. 6e. Since the structures in Figs. 6d and 6e are composites of existing molecular groups, no new absorption band is expected to appear in the infrared spectrum.

Consideration of the Spectral Intensities

Of the investigators who have employed infrared spectroscopy to study the alkali borates, only Moore and McMillan¹⁴ have attempted any quantitative treatment of their data. Based on their plots of

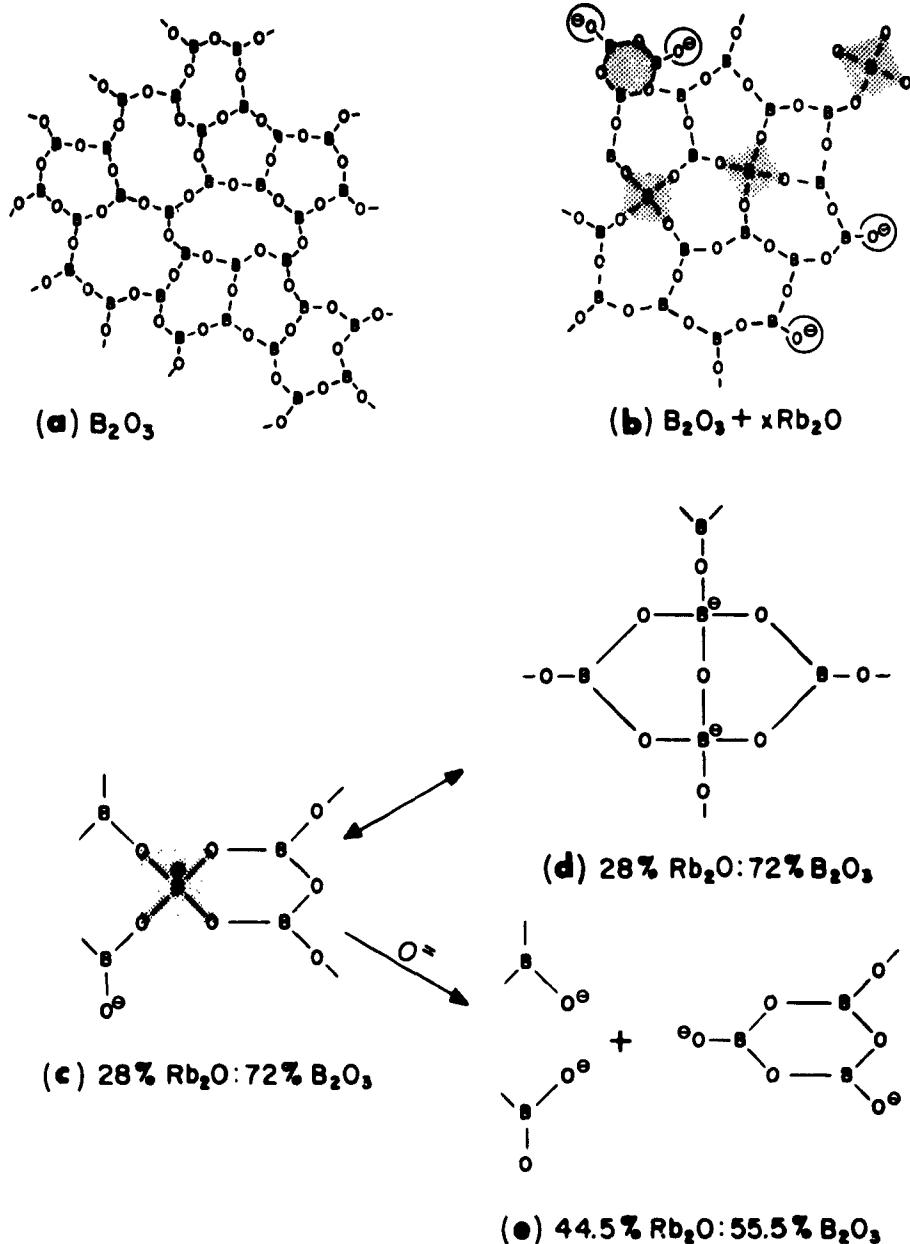


Fig. 6 Two-dimensional Schematic Representation of Rubidium Borate Structures at Various Rb_2O Concentrations

extinction-coefficient ratios vs. borate composition, they concluded that the proportion of BO_4^- groups in relation to BO_3^- increased progressively with added Na_2O until a borate contained approximately 17 mole % Na_2O , and that a further increase in alkali-oxide content caused no change in the $\text{BO}_4^-:\text{BO}_3^-$ ratio.

In this work, the 8-8.2- μ absorption band was used as the reference. The choice was not completely arbitrary, however, as the values of extinction ratios obtained were in conformance with the observed changes in spectra. Examination of Fig. 2 will show that a change in Rb_2O content from 28 to 33 mole % yields an unusually large change in relative intensities of the 7-7.5- μ and 8-8.2- μ bands. The graphs as plotted by Moore and McMillan apparently fail to show this. In order to facilitate comparison of their results with those from this work, experimental data from both studies are plotted together in Figs. 4A, 4B, and 4C.

It is seen that qualitatively the results are the same. An accelerated change does occur in the region of 28 to 30 mole % alkali oxide for all three borate glasses. Furthermore, the assumption from infrared spectral data that a discontinuity exists at 17 mole % alkali oxide is not justified. Also, alkali ion size is not of significant importance in modifying the borate glass structure.

At some alkali oxide concentration greater than 33 mole %, the tetrahedrally coordinated borons must revert to trigonal coordination. This process is in agreement with Krogh-Moe's theory.⁸ When conversion to crystalline rubidium metaborate is complete, all boron atoms are trigonally coordinated and incorporated into the boroxol structure.

Effect of Adding Complex-Forming Metals

Figure 5 shows the spectra of borate glasses to which oxides of different complex-forming metals - Nb_2O_5 , MoO_6 , V_2O_5 , TiO_2 , ZnO - have been added. Alteration of the original glass spectra is greatest in the borate of highest Rb_2O content. It may be recalled that the two absorption bands at 7-7.5 μ and 8-8.2 μ have been assigned to the $\text{B}-\text{O}^-$ group and the BO_3^- glass network, respectively.

If an equilibrium is presumed to exist between the two molecular groups in the borate glass, then a new equilibrium must be established upon addition of the metal oxides (Fig. 5B, 5C). Network reconstitution is favored, as evidenced by regression of the 7-7.5- μ band and enhancement of the 8-8.2- μ band. The degree of this change varies for glasses of different compositions and is greatest when the $\text{B}-\text{O}^-$

concentration is highest (at 33 mole % Rb₂O) and when the complexing strength of the added metal is highest. Relative values of complexing strength for these same metal ions have been determined by Adams and Quan¹ to be proportional to their ionization potentials and surface areas.

CONCLUSIONS

The experimental results of this study have shown that, contrary to many theoretical considerations of the vitreous alkali-borate structures, the glasses at any composition contain several molecular species. These are >B-O⁻ groups, BO₄⁻ groups, boroxol groups, and BO₃ groups. All increase proportionately with increasing Rb₂O content, except for BO₃ groups, which decrease due to collapse of the glass network structure. Between 28 and 33 mole % Rb₂O, this collapse is accelerated. At some concentration between 33 and 50 mole %, devitrification progressively takes place as tetrahedrally coordinated boron atoms revert to trigonal coordination.

In the infrared region of 2.5 to 15.5 μ , the lack of an observable discontinuity at the controversial composition of approximately 17 mole % Rb₂O indicates that no abrupt change occurs in the borate glass structure. Hence, a direct correlation between boron coordination and discontinuous physical properties at this concentration does not appear to be valid.

Support is found for the view that the borate glass network may be reconstituted by the introduction of certain metal ions which have the ability to enter into complex formation with singly-bonded oxygen atoms.

The oxides of rubidium, sodium, and lithium all affect the borate glass structure in the same manner, indicating the ion sizes of these alkali metals are of no consequence in determining borate glass structure.

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OF VARYING COMPOSITION

by J.T. Quan and
C.E. Adams 9 December 1963 30 p. tables
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The rubidium oxide concentration varied from 4.2 to 50 mole %. Frequency assignments were made for molecular (over)

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